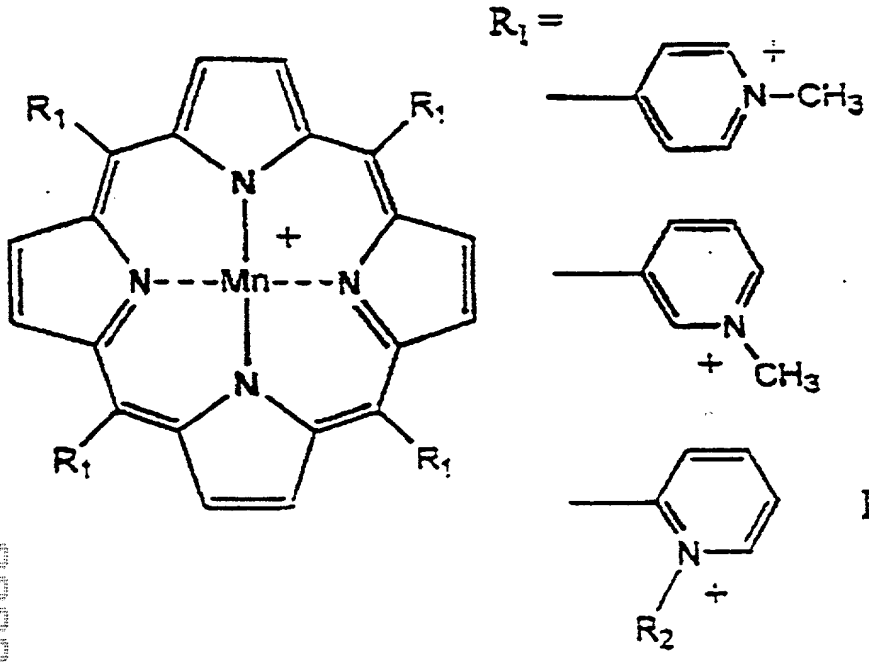
Figure 1

Mechanism

$$Mn(III)TMPyP + O_2^{\bullet} \rightarrow Mn(II)TMPyP + O_2$$

$$Mn(II)TMPyP + O_2^{-} + 2H^{+} \rightarrow Mn(III)TMPyP + H_2O_2$$



R_2 = $-CH_3$ 3 *ort*

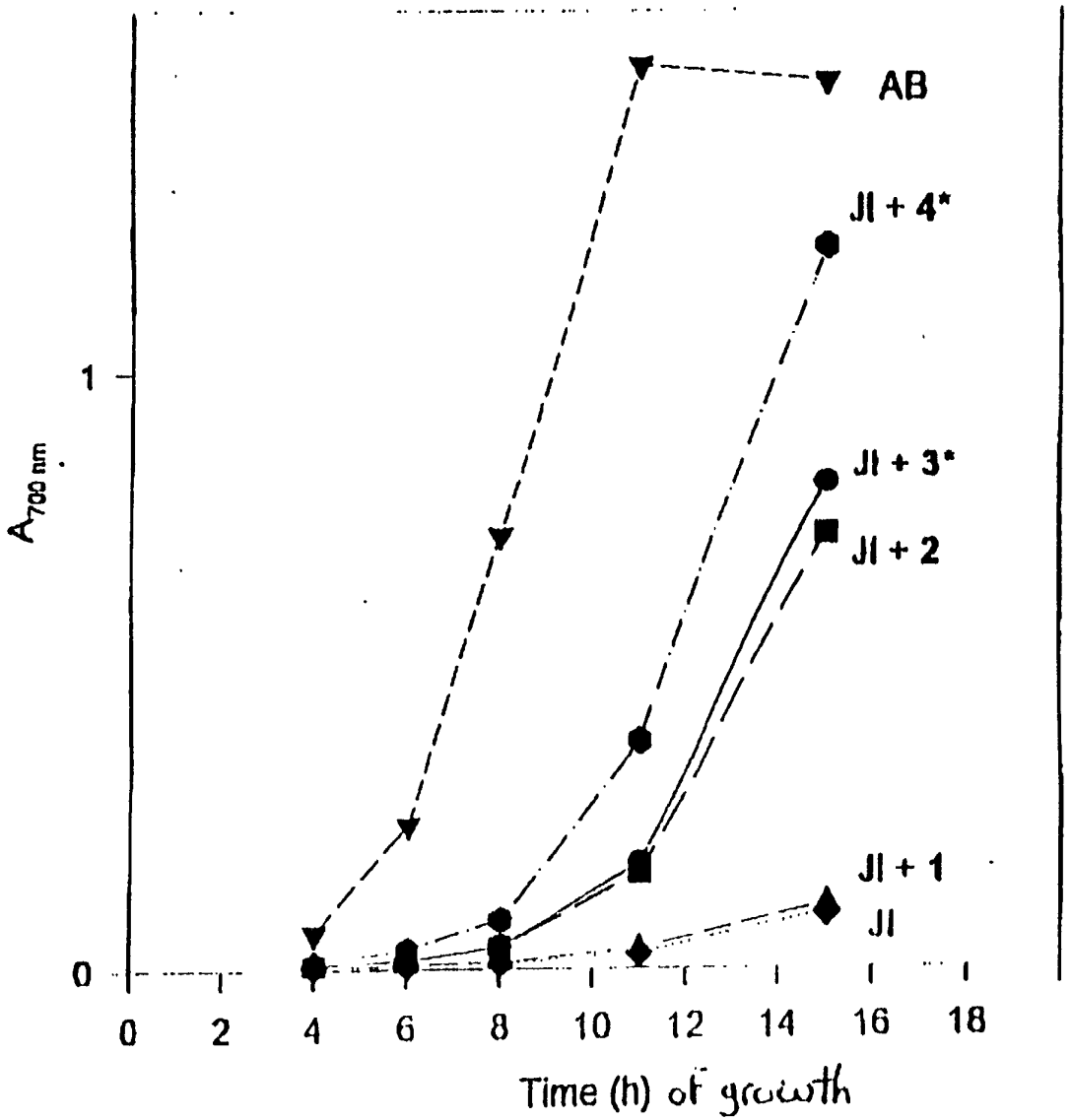
$-CH_2-CH_3$ 4

$-(CH_2)_3-CH_3$ 5

1 *par*

2 *me*

Figure 2. Manganese *meso*-tetraKis —*N*-alkyl-pyridinium based porphyr



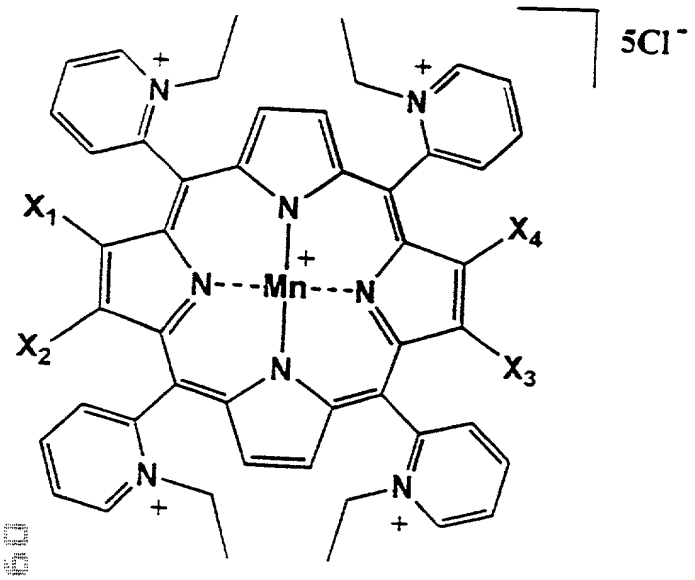
4 = ethyl version

3 = methyl in ortho position

2 = methyl in meta position

1 = methyl in para position.

Figure 3 SOD activity in *vivo* (*E. coli*) of **1**, **2**, **3*** and **4*** (25 μM) in minimal medium (*mixture of atropisomers, JI = SODs defficient strain, AB = parental strain).



$MnTE\text{-}2\text{-}PyP^{5+}$	$X_1=X_2=X_3=X_4=H$
$MnCl_1TE\text{-}2\text{-}PyP^{5+}$	$X_1=Cl$, $X_2=X_3=X_4=H$
$MnCl_{2a}TE\text{-}2\text{-}PyP^{5+}$	$X_1=X_2=Cl$, $X_3=X_4=H$
$MnCl_3TE\text{-}2\text{-}PyP^{5+}$	$X_1=X_2=X_3=Cl$, $X_4=H$
$MnCl_4TE\text{-}2\text{-}PyP^{5+}$	$X_1=X_2=X_3=X_4=Cl$

Figure 4

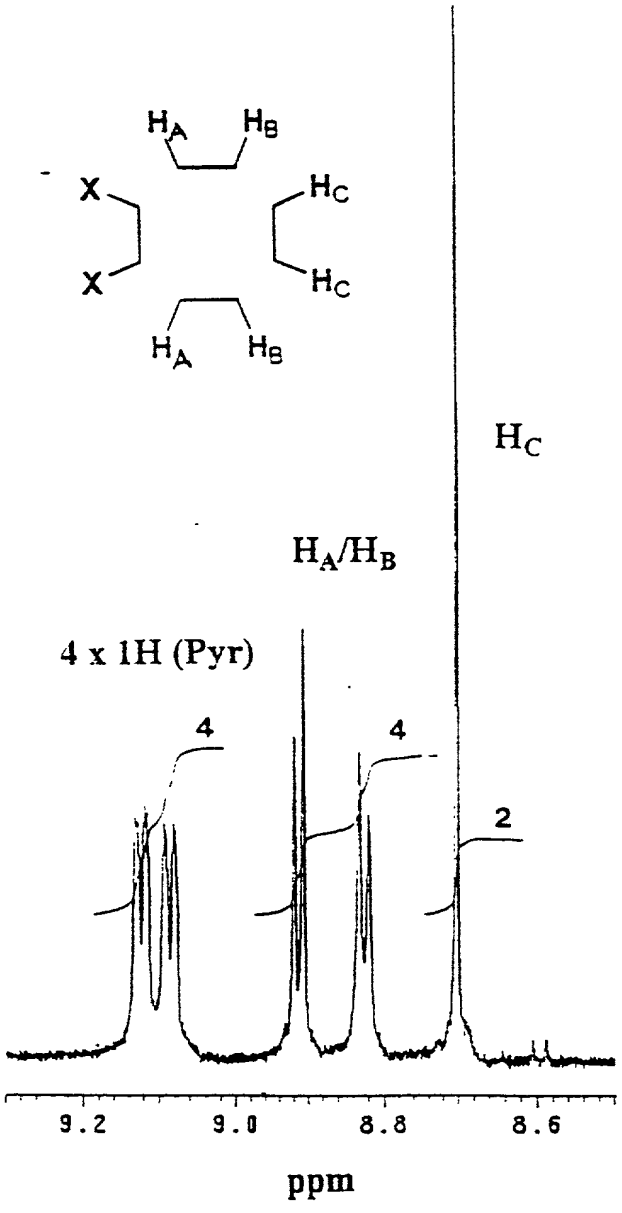


Figure 5

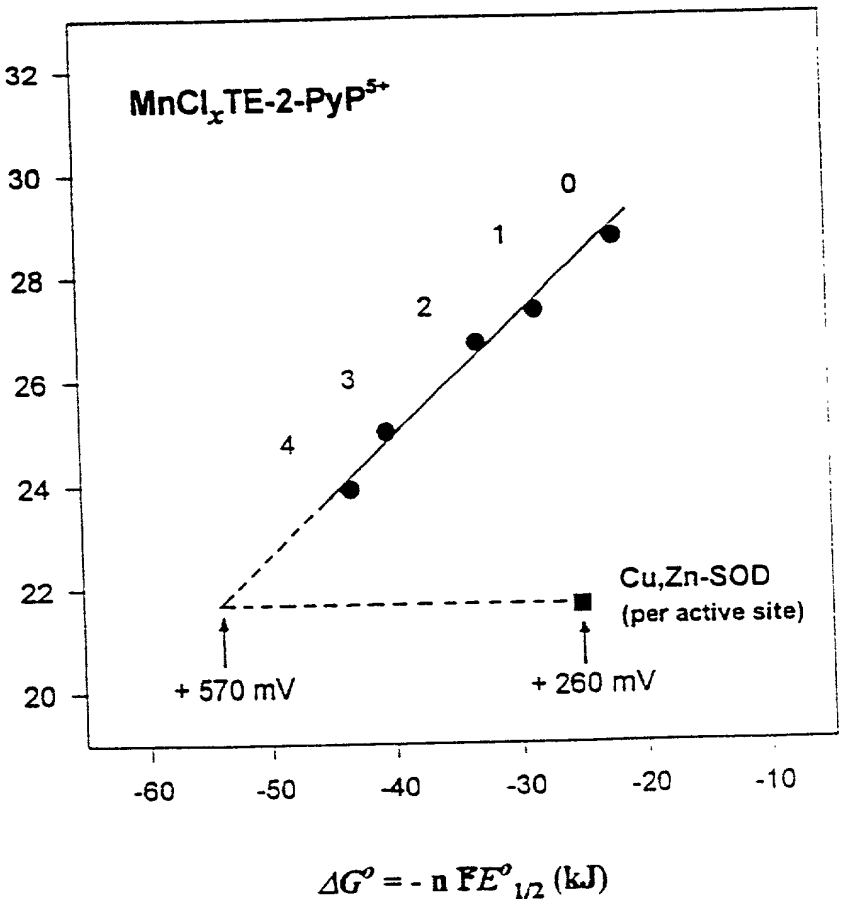
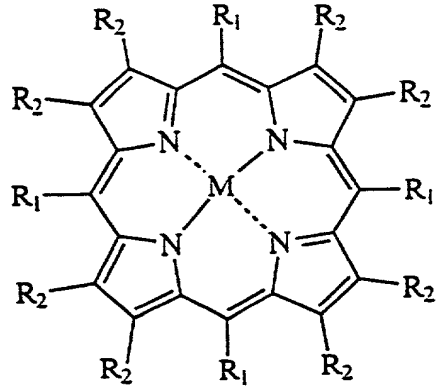
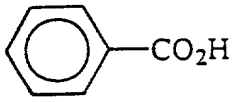
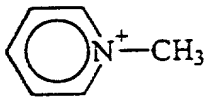
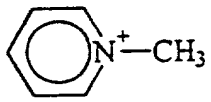
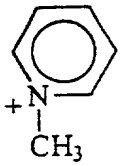

MnCl$_x$TE-2-PyP^{5+}
0
1
2
3
4
Cu,Zn-SOD
(per active site)
+ 570 mV
+ 260 mV
32
30
28
26
24
22
20
-60
-50
-40
-30
-20
-10
$\Delta G^{\#} = - RT.\ln(k_{cat}h/k_BT)$ (kJ)
$\Delta G^{\circ} = - n F E^{\circ}_{1/2}$ (kJ)

Figure 6

A

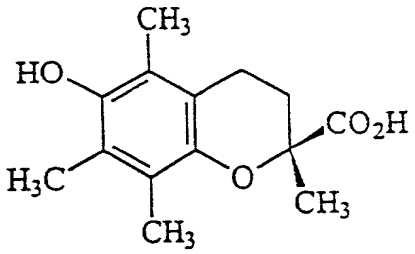


M= $Mn^{+2/+3}$, $Co^{+2/+3}$, $Fe^{+2/+3}$, or Zn^{+2}

R_1	R_2	
	H	**[TBAP]**
	H	**[TM-4-PyP]**
	Br	**[OBTM-4-PyP]**
	H	**[TM-2-PyP]**

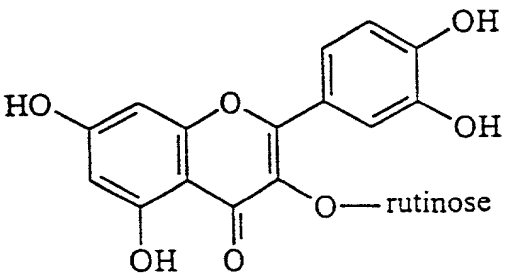
Metalloporphyrins

B



Trolox

C



(+)-Rutin

Figure 7

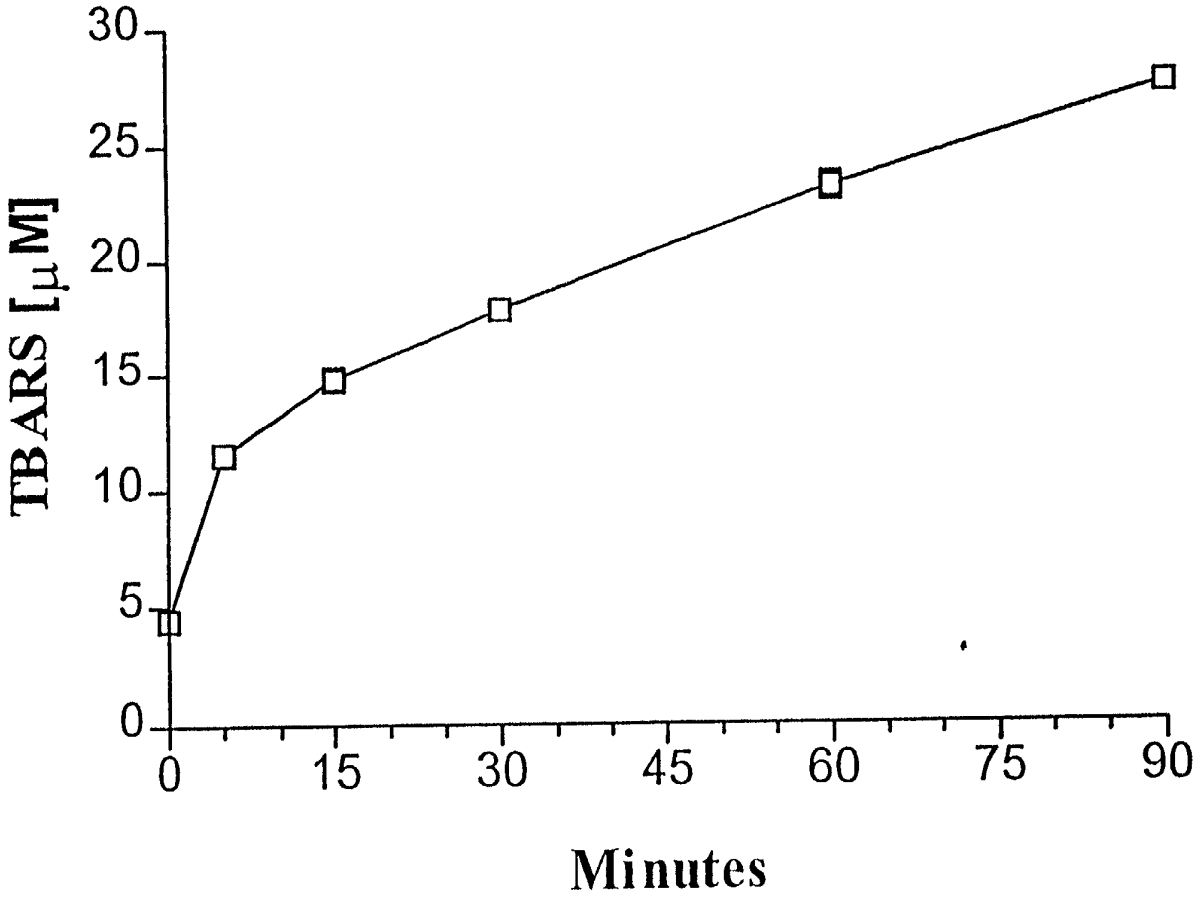


Figure 8

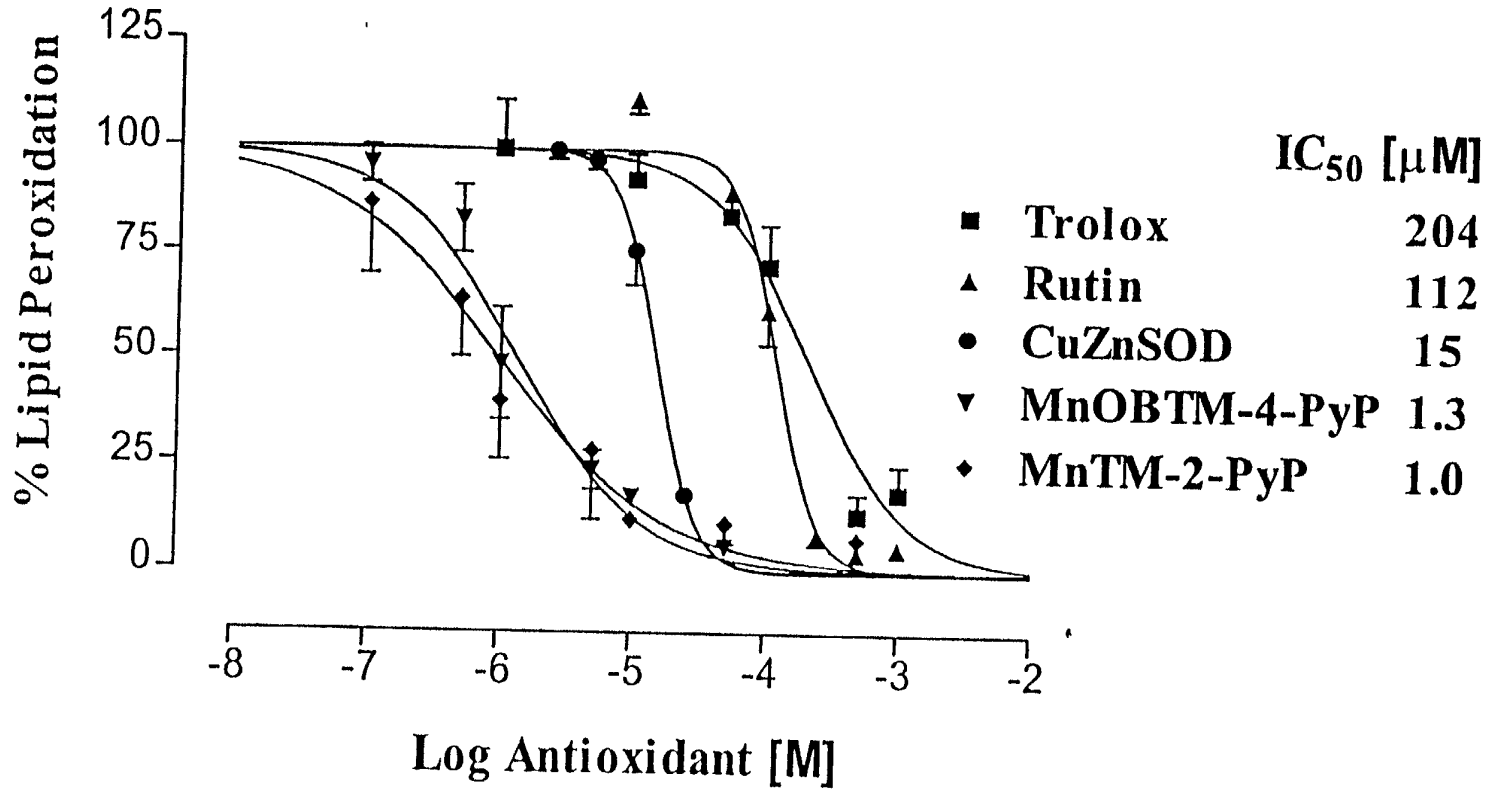


Figure 9

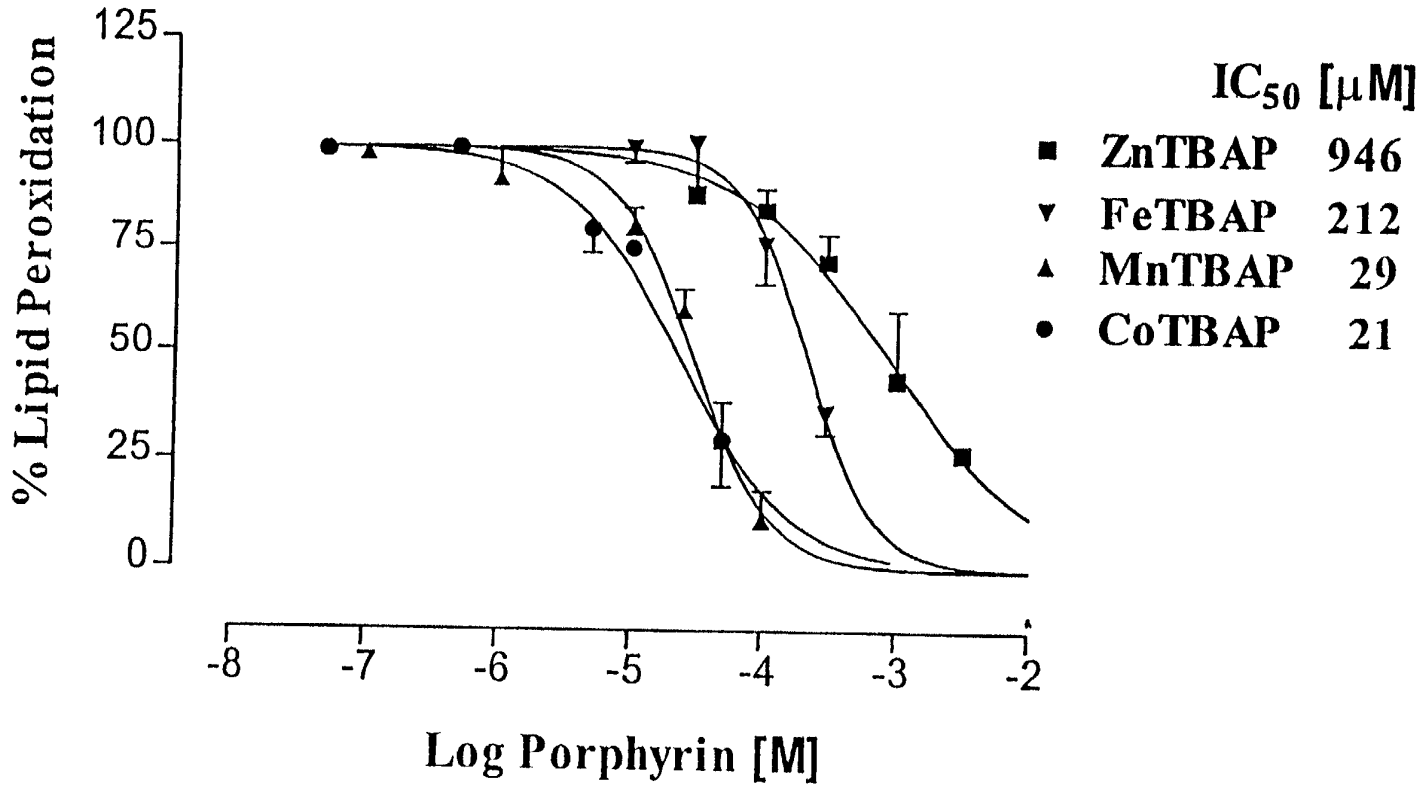


Figure 10

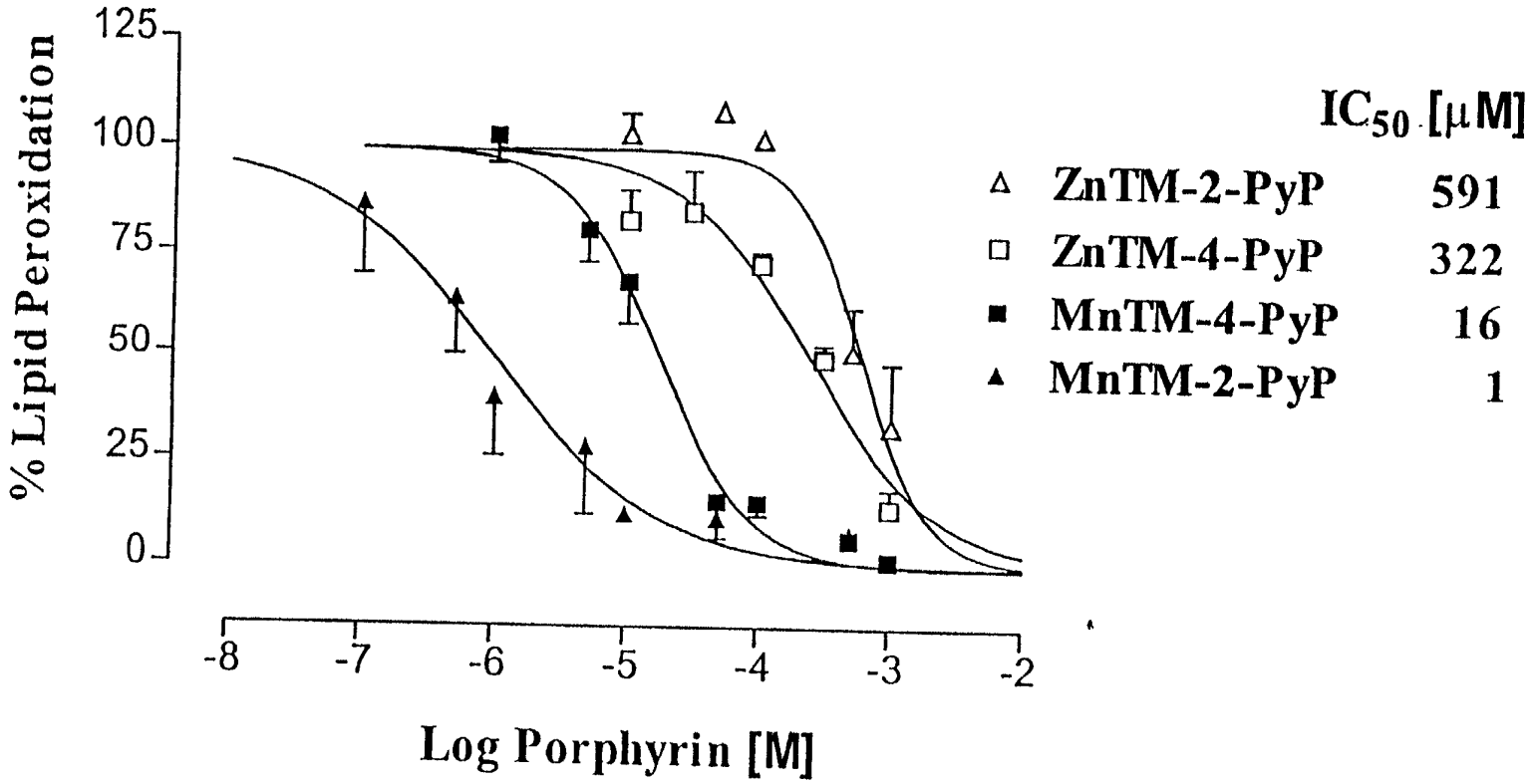


Figure 11